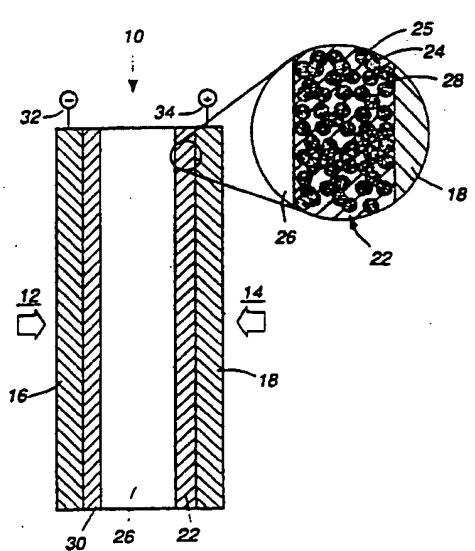


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p><b>(21) International Application Number:</b> PCT/US92/01058</p> <p><b>(22) International Filing Date:</b> 18 February 1992 (18.02.92)</p> <p><b>(30) Priority data:</b></p> <table border="0"> <tr> <td>656,329</td> <td>19 February 1991 (19.02.91)</td> <td>US</td> </tr> <tr> <td>736,876</td> <td>29 July 1991 (29.07.91)</td> <td>US</td> </tr> </table> <p><b>(71) Applicant:</b> UNITED STATES DEPARTMENT OF ENERGY [US/US]; 1000 Independence Avenue, S.W., Washington, DC 20585 (US).</p> <p><b>(72) Inventor:</b> WILSON, Mahlon, Scott ; 85 Mesa Verde, Los Alamos, NM 87544 (US).</p> <p><b>(74) Agents:</b> CONSTANT, Richard, E. et al.; United States Department of Energy, 1000 Independence Avenue, S.W., Washington, DC 20585 (US).</p>		656,329	19 February 1991 (19.02.91)	US	736,876	29 July 1991 (29.07.91)	US	<p><b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).</p> <p><b>Published</b> <i>With international search report.</i></p>
656,329	19 February 1991 (19.02.91)	US						
736,876	29 July 1991 (29.07.91)	US						
<p><b>(54) Title:</b> MEMBRANE CATALYST LAYER FOR FUEL CELLS</p> <p><b>(57) Abstract</b></p> <p>A gas reaction fuel cell (10) incorporates a thin catalyst layer (22) between a solid polymer electrolyte (SPE) membrane (26) and a porous electrode backing (18). The catalyst layer is preferably less than about 10 <math>\mu\text{m}</math> in thickness with a carbon supported platinum catalyst loading less than about 0.35 mgPt/cm<sup>2</sup>. The layer (22) is formed as an ink that is spread and cured on a film release blank. The cured film is then transferred to the SPE membrane (26) and hot pressed into the surface to form a catalyst layer (22) having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer (22) is formed by applying an Na<sup>+</sup> form of a perfluorosulfonate ionomer directly to the membrane (26), drying the film at a high temperature, and then converting the film back to the protonated form of the ionomer. The layer (22) has adequate gas permeability so that cell performance is not affected and has a density and particle distribution effective to optimize proton access to the catalyst and electronic continuity for electron flow from the half-cell reaction occurring at the catalyst.</p>  <p>The diagram shows a cross-section of a fuel cell (10) with two porous electrode backings (18) separated by a solid polymer electrolyte (SPE) membrane (26). A thin catalyst layer (22) is positioned between the membrane (26) and the electrode backings (18). The catalyst layer (22) is formed by applying an ink to the membrane (26) and hot pressing it into the surface. A magnified view of the catalyst layer (22) shows a porous structure with catalyst particles (24) and a perfluorosulfonate ionomer (25) matrix. The catalyst layer (22) is formed by applying an ink to the membrane (26) and hot pressing it into the surface. The diagram also shows the flow of reactants (12, 14) into the cell and the flow of products (16, 18) out of the cell.</p>								

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## MEMBRANE CATALYST LAYER FOR FUEL CELLS

RELATED CASES

This application is a continuation-in-part of U.S. Patent application S.N. 07/656,329, filed February 19, 1991.

BACKGROUND OF INVENTION

05 This invention relates to fuel cells and, more particularly, to catalyst loadings for solid polymer electrolyte fuel cells. This invention is the result of a contract with the Department of Energy (Contract No. 10 W-7405-ENG-36).

Fuel cells are energy conversion devices presently being considered as one alternative to internal combustion engines. One type of fuel cell uses a solid polymer electrolyte (SPE) membrane, or proton exchange membrane, to 15 provide ion exchange between the cathode and anode electrodes. Gaseous fuels may be used within the fuel cell, particularly hydrogen ( $H_2$ ) and oxygen ( $O_2$ ), where the electrodes are formed of porous conductive materials, e.g., woven graphite, to enable the fuel to disperse over 20 the face of the SPE.

SPE fuel cells offer many advantages over liquid electrolyte fuel cells, including greater ultimate power densities, lower operating temperatures, and longer operating lifetimes. SPE materials are also generally 25 resistant to corrosion and easy to incorporate into fuel cell structures. However, the anode and cathode half-cell

reactions,  $H_2$  and  $O_2$  reactions, respectively, require catalysts to proceed at useful rates. As described in U.S. Patent 4,876,115, issued October 24, 1989, and incorporated herein by reference, catalyst materials were first  
05 incorporated by hot pressing the materials directly into the surface of the SPE membrane. Useful current densities in conventional SPE fuel cells were achieved only with high catalyst loadings, e.g.,  $4 \text{ mg Pt/cm}^2$ . Since the catalyst materials are from the platinum group, with platinum being  
10 the preferred catalyst, these SPE fuel cells (herein referred to as GE/HS-UTC-type fuel cells) have not been cost competitive with other energy sources.

The '115 patent is directed to reducing the required platinum loading where the platinum is provided as platinum  
15 loaded carbon particles on a carbon cloth or carbon paper electrode substrate bound together by a hydrophobic component, such as polytetrafluorethylene (PTFE). The catalyzed sides of the carbon electrodes are impregnated to a depth of about  $10 \text{ } \mu\text{m}$  with a solubilized form of the  
20 SPE to increase the access of the electrolyte to the platinum within the Pt-C/teflon catalyst layer. Indeed, catalyst loadings down to  $0.35 \text{ mg/cm}^2$  of SPE area are reported to provide performance equivalent to conventional fuel cell catalyst loadings of  $4 \text{ mg/cm}^2$ .

25 The platinum catalyst is, however, not efficiently utilized in the prior art structures. It is difficult to match the impregnation depth of the SPE with the erratic thickness of a typical catalyst layer. This results in areas that are not fully impregnated and other areas where  
30 the SPE material extends deeper into the electrode than the catalyst layer and impedes gas diffusion through the electrode. Further, the hydrophobic binder blocks proton and oxygen access to catalyst sites in cathode electrodes.

SUBSTITUTE SHEET

Another problem with prior art fuel cells is differential swelling between the SPE and the catalyst layer arising from the differing hydration characteristics between the hydrophilic SPE membrane and the carbon-based electrode structure. Delamination can occur between the SPE membrane and the electrode with a resulting discontinuity in the ion path and decreased cell longevity.

These problems are addressed by the present invention and a catalyst layer is provided adjacent a fuel cell SPE that is hydrophilic, contains substantially no cavities, is uniformly thin, and contains a uniform ratio of binder ionomer to supported catalyst.

Accordingly, it is an object of the present invention to provide a SPE fuel cell with relatively low supported catalyst loadings with no reduction in performance.

It is another object of the present invention to provide uniform continuity of electronic and ionic paths about all of the catalyst sites.

Still another object of the present invention is to provide a uniform dispersion of the supported catalyst layer in the binder layer.

One other object of the present invention is to improve the bonding between the SPE membrane and the catalyst layer.

Yet another object of the present invention is to provide a thin catalyst layer for adequate oxygen transport to all the catalyst sites through the ionomer binder material.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may

be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

#### SUMMARY OF THE INVENTION

05 To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the apparatus of this invention may comprise a gas reaction fuel cell having  
10 a solid polymer electrolyte for separating anodic and cathodic electrodes, wherein the improvement comprises a film of a proton conducting material with a thickness less than about 10  $\mu\text{m}$  and having a supported platinum catalyst uniformly dispersed therein with a platinum  
15 loading less than about 0.35  $\text{gm}/\text{cm}^2$ , where said film is disposed between the solid polymer electrolyte and at least the cathodic electrode. A preferred film thickness is less than 5  $\mu\text{m}$ .

In another characterization of the present invention, a  
20 SPE fuel cell using hydrogen and oxygen is formed with a catalyst layer fabricated as a separate unit. A selected loading of supported Pt catalyst is uniformly dispersed in an ionomer that is effective for oxygen permeation and for ion transport, where the resulting mixture is formed as a  
25 thin film. The thin film is then transferred to the surface of a SPE membrane. The fuel cell is completed by urging a porous electrode structure against the catalyst film for oxygen transport through the ionomer to the catalyst sites.

In yet another characterization of the present invention, a SPE fuel cell using hydrogen and oxygen is formed using a  $\text{Na}^+$  form of a perfluorosulfonate ionomer to fabricate a catalyst layer. A supported Pt catalyst and a solvent are uniformly blended with the  $\text{Na}^+$  form of the ionomer to form an ink. The ink is applied to form a layer over a surface of the SPE membrane, also in the  $\text{Na}^+$  form. The layer is then dried at a temperature of at least  $150^\circ\text{C}$  for a time effective to dry the ink. The resulting film and membrane are converted back to the protonated form of the ionomer to form a pliant, elastic, and coherent catalytic layer on the SPE membrane.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate an embodiment of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

FIGURE 1 is a cross section of a fuel cell having a structure in accordance with one embodiment of the present invention.

FIGURE 1A is a pictorial illustration showing a magnified view of the catalyst layer according to the present invention.

FIGURE 2 graphically depicts the performance of a thin catalyst film with  $0.20 \text{ mg/cm}^2$  and a thicker catalyst film with  $0.35 \text{ mg/cm}^2$  of platinum on a first SPE.

FIGURE 3 graphically compares performance of thin catalyst films with  $0.15$  and  $0.22 \text{ mgPt/cm}^2$  on a second SPE.

FIGURE 4 graphically compares the performance of a thin film cathode according to the present invention with 0.15 mgPt/cm<sup>2</sup> and a commercial gas-diffusion cathode with 0.35 mgPt/cm<sup>2</sup>.

05 FIGURE 5 graphically depicts the performance of a fuel cell with a high-temperature formed, thin film catalyst layer with 0.17 gm Pt/cm<sup>2</sup>/electrode on Membrane "C".

FIGURE 6 graphically depicts the performance of a fuel cell with a high temperature formed, thin film catalyst layer with 0.13 mg Pt/cm<sup>2</sup>/electrode on a Dow membrane.

10 FIGURE 7 graphically compares the specific activity from a fuel cell according to the present invention and prior art fuel cells.

#### DETAILED DESCRIPTION OF THE INVENTION

15 In accordance with the present invention, a gas reaction fuel cell includes a catalyst layer adjacent the cathode surface of a solid polymer electrolyte membrane to optimize utilization of the catalyst and to minimize the amount of the included catalyst. As shown in Figures 1 and 1A, catalyst layer 22 addresses three criteria necessary for a catalyst to efficiently contribute to the electrochemical processes in a fuel cell: proton access to the catalyst, gas access, and electronic continuity.

20 Fuel cell assembly 10 utilizes a gas fuel source 12, gas oxidizer source 14, solid polymer electrolyte (SPE) membrane 26 between porous anode backing structure 16 and porous cathode backing structure 18, and at least catalyst layer 22, according to the present invention, between the cathode surface of SPE 26 and cathode backing 18. It will be understood that catalyst layer 30 may be disposed between membrane 26 and anode backing structure 16. The

25  
30



foregoing discussion applies also to catalyst layer 30, although catalyst loadings for the anode may be only about one-half the catalyst loadings required for the cathode structure. Catalyst layer 22 is formed as a film of an  
05 proton conductive ionomer 28 and a supported platinum (Pt) catalyst 24 uniformly dispersed in ionomer 28 to assure that a uniform and controlled depth of the catalyst is maintained. The resulting film is a dense film of ionomer  
10 28 and supported catalyst 24, i.e., there are no substantial voids in the film and there are no hydrophobic additives, such as PTFE, that block access of the diffusing gas and protons to the Pt catalyst sites. Gas access to the Pt catalyst sites is obtained through porous cathode backing structure 18 and by diffusion through ionomer 28.  
15 A suitable ionomer, such as a perfluorosulfonate ionomer, has sufficient oxygen permeability that a diffusion pathway length of 5-10  $\mu\text{m}$  does not introduce any significant oxygen transport losses through the film for an oxygen gas.

Proton penetration and gas diffusion effects of  
20 electrolyte layers, as well as the relationship between volume fraction of ionomer 28 and potential drop within catalyst layer 22, indicate that an optimum catalyst layer 22 is very thin, i.e., less than 10  $\mu\text{m}$ , and has a high volume density of supported catalyst 24 with the ionomer 28  
25 in the interstices, i.e., the supporting carbon particles 25 are in contact with adjacent particles to form a low resistance electronic path through catalyst layer 22. A weight ratio of about 1:3 perfluorosulfonate ionomer (dry)/Pt-C is preferred for 20 wt% supported Pt. A dense  
30 film 22 is formed that is substantially free of cavities or water pockets that will lower the ionic and electronic conductivities. It will be appreciated that the thickness

of film 22 is optimized when the thickness is equal to the active region for the half-cell reaction at any given current density and may be selected on the basis of the expected operating characteristics to match the catalyst thickness with a predetermined operating current density.

05 In one embodiment, film 22 is formed from an ink preparation including the supported catalyst, a solubilized ionomer, and one or more volatile or decomposable suspension materials to provide a viscosity suitable for  
10 film formation. The ink is spread over a release blank in one or more layers to provide a preselected concentration of catalyst. A preferred protocol is as follows:

#### PROTOCOL I

1. Combine a solubilized perfluorosulfonate ionomer,  
15 such as Nafion (a registered trademark of E.I. duPont Nemours) in 5% solution (from Solution Technology, Inc.) and a supported catalyst (19.8 wt % platinum on carbon from Prototech Company, Newton Highlands, Massachusetts) in a weight ratio of 1:3 Nafion (dry)/Pt-C.
2. Add water and glycerol to weight ratios of about  
20 1:5:20 for carbon/water/glycerol.
3. Agitate the mixture with ultrasound to uniformly disperse the supported catalyst in the ink and to form the mixture to a viscosity suitable for coating the release  
25 blank.
4. Clean a release blank of teflon film and coat the blank with a thin layer of mold release (e.g., a TFE spray). Paint the blank with a layer of ink and bake in an oven at 135°C until dry. Add layers until the desired  
30 catalyst loading is achieved.

5. Form an assembly of a polymer electrolyte membrane, counter electrode (anode electrode), and the coated blank. Place the assembly into a conventional hot press and lightly load the press until the press heats to a selected temperature (i.e., 125°C for Nafion and 145°C for "C" SPE material) and then press at 70-90 atm for 90 seconds.

6. Cool the assembly and then peel the release blank from the film, leaving the film adhered to the SPE membrane cathode surface.

7. An uncatalyzed porous electrode (Prototech) is urged against the films during fuel cell assembly to form a gas diffusion backing for the thin film catalyst layer.

It should be recognized that the solubilized Nafion acts to some extent as a surfactant and dispersing agent for the supported catalyst particles. However, the dispersion of the Nafion must be controlled to provide a suitably dense film. An effective density for the present invention is obtained by simply mixing the Pt-C particles and solubilized Nafion together before the water and glycerol mixture is added.

One advantage of the dense catalyst layer herein described is improved bonding of the catalyst layer to the SPE membrane and continuity of the proton path. The dimensions of the SPE membrane increase considerably upon hydration of the hydrophilic material, whereas the relatively rigid carbon matrix of conventional gas-diffusion electrode structures does not significantly change dimensions upon hydration. Thus, where the catalyst is included within the carbon electrode structure, the continuity between the SPE surface and the catalyst interface can be adversely affected. The dense catalyst layer according to the present invention includes a

hydrophilic material as a large fraction of the catalyst layer and there is less differential movement from surface expansions under hydration.

05 One disadvantage of forming the catalyst layer without a binder material, such as PTFE, is that suitable ionomer materials, such as Nafion, must provide structural integrity for the layer. Nafion, for example, is not melt processable and the resulting recast catalyst layer films do not have the structural integrity of commercial  
10 fluoropolymer SPE membranes. It has been found, however, that the structural integrity can be improved by heating the film to elevated temperatures for moderate amounts of time. This does cause some amount of acid-catalyzed discoloration and degradation, but the increase in  
15 structural integrity is beneficial. The film is also rendered somewhat less hydrophilic by the heating, which is beneficial at the cathode electrode where water flooding is of concern. A suitable treatment is thirty minutes exposure at 130-135°C.

20 Another approach to improve the structural integrity of the catalyst layer film is to introduce a binder material that readily disperses throughout the electrode structure and imparts structural integrity at low volume fractions such that performance of the electrode is not significantly  
25 impaired. Useful catalyst layers have been prepared using polyvinyl alcohol (PVA) in place of the glycerol in forming the ink. The surfactant nature of the PVA provides for adequate dispersion among the supported catalyst particles and the molecular structure acts to bind the carbon  
30 particles and Nafion agglomerates so that strong films are obtained with low weight fractions of PVA. Films have been formed with PVA concentrations of 10-12 wt% in the ink.

In another embodiment of the present invention, the integrity of catalyst layers 22, 30 is improved and acid-catalyzed degradation of the ionomer is avoided by using the  $\text{Na}^+$  form of the perfluorosulfonate ionomer, i.e., Nafion, to form a film for application to membrane 26 or for direct application to membrane 26, where membrane 26 is in a  $\text{Na}^+$  or  $\text{K}^+$  form. The  $\text{Na}^+$  perfluorosulfonate layer is cured at a temperature of at least  $150^\circ\text{C}$ , and preferably at least  $160^\circ\text{C}$ , and the catalyzed membrane assembly is thereafter converted to the  $\text{H}^+$ , i.e., protonated, form to complete the catalyzed membrane assembly. A preferred protocol is as follows:

## PROTOCOL II

1. Prepare a mixture of Nafion and catalyst as described in Step 1 of Protocol I.
2. Add a molar amount of  $\text{NaOH}$  equal to the Nafion and mix well to convert the Nafion to the  $\text{Na}^+$  form.
3. Form an ink as in steps 2 and 3 of Protocol I.
4. Provide a membrane of  $\text{Na}^+$  Nafion by soaking a protonated membrane in a solution of  $\text{NaOH}$ , followed by rinsing and drying, or by procuring the membrane in a  $\text{Na}^+$  or  $\text{K}^+$  form.
5. Apply the ink directly to one side of the membrane. The amount of catalyst applied to the membrane is determined from the amount of ink transferred to the surface. Typically, two coats are required to obtain the desired catalyst loading. In one method of drying the ink, the ink-coated membrane is placed on a vacuum table having a fine sintered stainless steel filter on top of a heated vacuum manifold plate. A silicone blanket having a cut-out area the size of the membrane area to be inked is placed over the membrane to seal the uncovered areas of the vacuum

table about the membrane. The vacuum table is operated at a temperature of at least 150°C, and preferably about 160°C, as the ink is applied. The vacuum appears to prevent distortion of the membrane from solvents in the ink and to yield a smooth, uniform film. The high-temperature application and drying appears to cure the catalyst layer to a film of high integrity and that is pliant and elastic. The second side of the membrane may be coated in the same manner.

10 6. Optionally, the assembly is hot pressed at 70-90 atm at 185°C for about 90 seconds.

7. The assembly is converted back to the protonated form by lightly boiling it in 0.1M H<sub>2</sub>SO<sub>4</sub> and rinsing in deionized water. The assembly is air dried and combined with an uncatalyzed porous electrode as in Step 7 of Protocol I.

Alternately, the Na<sup>+</sup> form of ink (Steps 1-3, above) and membrane may be used in Protocol I to form a separate catalyst film for application to the membrane.

20 The high-temperature casting of Na<sup>+</sup> Nafion films to improve film integrity is generally suggested in Moore et al., "Procedure for Preparing Solution-Cast Perfluorosulfonate Ionomer Films and Membranes," 58 Anal. Chem., pp. 2569-2570 (1986), incorporated herein by reference. The article suggests that solvents such as dimethyl sulfoxide (DMSO) might yield equivalent properties to glycerol solvents, described above, but at lower process temperatures. The above protocol appears to yield equivalent cell performance with both DMSO and glycerol solvents. DMSO does provide a good suspension medium for the solids, however, and may form a good solution for a spray application of ink to the membrane surface.

Figures 2-7 graphically depict the performance of fuel cells prepared according to the present invention. All of the ink formulations were prepared using supported catalysts of 19.8 wt% platinum on XC-72 carbon powder (Prototech) mixed with Nafion. The cathode electrodes for mating with the catalyst layer were conventional PTFE bonded electrodes with no catalyst (Prototech). The fuel cells whose performance is shown in Figures 1-4 have cathodes prepared according to Protocol I and include conventional anodes (Prototech) with a catalyst loading of 0.35 mg Pt/cm<sup>2</sup> plus a sputter coat of 500 Å Pt. It will be understood that conventional anode electrodes were used to provide performance comparisons of cathode electrodes.

The anode catalyst loading is not expected to have any significant effect on cell performance. Indeed, the fuel cells whose performance is shown in Figures 5 and 6 include high temperature catalytic layers on both the cathode and anode faces of the membrane. both catalytic layers incorporated equivalent catalyst loadings, e.g., 0.13 mg Pt/cm<sup>2</sup>, for a total cell loading of, 0.26 mg Pt/cm<sup>2</sup> of electrode surface.

Figure 2 graphically depicts the voltage vs. current density curves for fuel cells having conventional Prototech anodes, Nafion 117 (7 mil thick) SPE membrane, and a cathode assembly with a catalyst layer produced by mixing Pt/C catalyst and Nafion and hot pressed onto the SPE membrane. Catalyst loadings of 0.20 and 0.35 mg Pt/cm<sup>2</sup> are compared using both neat oxygen and air as the oxidant. It is readily seen that the thinner catalyst layer (0.20 mg Pt/cm<sup>2</sup>) performs somewhat better than the

thicker film ( $0.35 \text{ mg Pt/cm}^2$ ) at higher current densities. At the higher current densities, the active region of the catalyst layer narrows and less of the film thickness is utilized, wherein mass transfer losses increase in the thicker film and performance decreases. The low partial pressure of oxygen in air as compared to neat oxygen induces an earlier and steeper fall off in performance at the higher current densities.

Figure 3 graphically depicts the voltage vs. current density curves for fuel cells constructed as the fuel cells of Figure 2, except that the SPE membrane is Membrane "C" (a perfluorosulfonate membrane from Chlorine Engineers Inc. of Japan). Catalyst loadings of  $0.15$  and  $0.22 \text{ mg Pt/cm}^2$  are compared, again using both neat oxygen and air as oxidizers. The results are consistent with the results shown with Nafion 117 forming the SPE membrane, with lower potentials from the thicker film at higher current densities.

The performance of the fuel cells depicted in both Figures 2 and 3 approach those of fuel cells fabricated with conventional Prototech cathode assemblies or of assemblies using unsupported Pt catalyst with much higher Pt loadings. Figure 4 particularly compares the cell voltage vs. current density performance of a thin catalyst with a loading of  $0.15 \text{ mg Pt/cm}^2$  with a cell having the catalyst included in a carbon electrode to a loading of  $0.35 \text{ mg Pt/cm}^2$  with an extra sputter coating of  $500 \text{ \AA}$  Pt. The substantial similarity in performance is readily apparent.

The performance of fuel cells formed by a direct application of a  $\text{Na}^+$  ink to a  $\text{Na}^+$  membrane is shown in Figures 5 and 6. Figure 5 depicts the performance of the



high-temperature, thin film formed on Membrane "C" according to Protocol II, wherein the cell performance on oxygen is at least equal to the performance of the separate thin film cell shown in Figure 4. Figure 6 depicts the performance of the high-temperature, thin film formed on a "Dow" membrane according to Protocol II, wherein an improved cell performance is obtained. The "Dow" membrane is a proton conducting membrane available from the Dow Chemical Company. It is quite significant that a low Pt loading of  $0.13 \text{ mg Pt/cm}^2$  is effective to generate current densities of above  $3 \text{ A/cm}^2$  at a cell voltage higher than  $0.4\text{V}$  for operation on pressurized oxygen and, particularly, that such a low loading is effective to reach a cell voltage of  $0.65\text{V}$  at  $1 \text{ A/cm}^2$  for cells operated on pressurized air.

To further illustrate the significant increase in catalyst utilization efficiency afforded by the present invention, Figure 7 depicts cell voltage as a function of the specific activities of the cathodes ( $\text{A/mgPt}$ ) for fuel cells with four different cathode catalyst configurations: (1) a thin film catalyst loading of  $0.15 \text{ mg Pt/cm}^2$ , as taught herein; (2) a high-temperature thin film with a catalyst loading of  $0.13 \text{ mg Pt/cm}^2$  applied directly to the membrane as an ink; (3) a commercial Prototech electrode with a catalyst loading of  $0.35 \text{ mg Pt/cm}^2$  and  $500 \text{ \AA}$  Pt coating; and (4) GE/HS-UTC-type cell with  $4 \text{ mg Pt/cm}^2$  (unsupported) hot pressed into the SPE. It should be noted that the GE/HS-UTC-type cell has hardware, membrane design, and operating conditions that are significantly different from the other cells and its performance comparison is merely illustrative. The differences in the specific activities for each type of

electrode are clearly significant, with the thin film supported catalyst layers according to the present invention being the most efficient utilization of the Pt catalyst.

05 Thus, it will be appreciated that the present invention obtains a high catalyst utilization by the improved construction of the catalyst layer with low Pt loadings primarily involving increased contact area between the polymer electrolyte and the Pt catalyst clusters. The  
10 contact area is increased in two ways. First, the supported catalyst and the ionomeric additive are cast together to form the catalytic layer. Second, the hydrophobic additive is completely eliminated and the ionomer is uniformly dispersed throughout the catalyst  
15 layer. The latter is accomplished by blending the solubilized ionomer and the platinized carbon into a homogeneous "ink," from which the thin film catalyst layer is formed.

Figures 2 and 3 illustrate the significance of film  
20 thickness affecting proton penetration and gas access and the resulting cell performance. As current density increases, the active catalyst region narrows. Thus, the oxidizer gas must diffuse through the inactive portion of the catalyst layer and, in the case of air, the mass  
25 transfer limitation significantly increases the overpotential. An electrode thickness roughly equivalent to that of the active region at a particular current density would provide an optimum performance at that current density. For example, with 20 wt% Pt/C supported  
30 catalyst and a catalyst layer fabricated in accordance with the above principles, reasonable fuel cell performance is obtained down to about 0.1 mg Pt/cm<sup>2</sup>, after which it

falls off in proportion to further decrease in catalyst loading. Concomitant film thicknesses are in the range of 1-10  $\mu$ , and preferably 2 to 3  $\mu$ . It is expected that catalyst loadings as low as 0.05 mg Pt/cm<sup>2</sup> may be used for an anode catalyst layer without significant loss of performance. Improved performance might be obtained from a given catalyst layer thickness if a higher Pt loading could be included without increasing the thickness of the supported catalyst.

10 The foregoing description of the preferred embodiments of the invention have been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The  
15 embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with  
20 various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

## WHAT IS CLAIMED IS:

05 1. A gas reaction fuel cell having a solid polymer electrolyte for separating anodic and cathodic electrodes, wherein the improvement comprises a composite film of a supported platinum catalyst and a proton conducting ionomer with a thickness less than about 10  $\mu\text{m}$ , said catalyst being uniformly dispersed therein with a platinum loading less than about 0.35 mgPt/cm<sup>2</sup>, where said film is disposed between said solid polymer electrolyte and at least said cathodic electrode.

2. A gas reaction fuel cell according to Claim 1, where said platinum loading is greater than 0.1 mg/cm<sup>2</sup>.

3. A gas reaction fuel cell according to Claim 1, wherein said proton conducting material is the same material forming said solid polymer electrolyte.

05 4. A gas reaction fuel cell according to Claim 1, wherein said film of proton conducting ionomer is formed from a perfluorosulfonate ionomer by drying at a temperature of at least 150°C a solution containing a Na<sup>+</sup> form of said ionomer and thereafter converting said Na<sup>+</sup> form to a protonated form.

5. A method according to Claim 1, wherein the step of transferring said film comprises the steps of:  
forming said film over a release blank to a selected catalyst loading;

05 hot pressing said film into said surface of said solid polymer electrolyte to cure said film and adhere said film to said surface; and

removing said release blank from said film.

6. A method according to Claim 5, wherein the step of dispersing said catalyst in said ionomer further includes the steps of:

05 adding a solvent to said ionomer and said catalyst to obtain a mixture with a viscosity effective for forming said film; and

agitating said mixture to disperse said catalyst.

7. A method for fabricating a gas reaction fuel cell having a solid polymer electrolyte for separating anodic and cathodic electrodes, comprising the steps of:

05 uniformly dispersing a supported Pt catalyst in a perfluorosulfonate ionomer;

forming a thin film of said ionomer with said catalyst;

transferring said film to a surface of said solid polymer electrolyte; and

10 urging a porous electrode structure against said film to form at least said cathodic electrode.

8. A method according to Claim 7, further including the step of furnishing said perfluorosulfonate ionomer in a  $\text{Na}^+$  form.

9. A method according to Claim 8, further including the step of furnishing said membrane as a perfluorosulfonate material in a  $\text{Na}^+$  or  $\text{K}^+$  form.

10. A method according to Claim 8, further including the step of converting said thin film of said ionomer to a protonated form of said ionomer.

11. A method according to Claim 7, wherein the step of transferring said film comprises the steps of:

forming said film over a release blank to a selected catalyst loading;

05 hot pressing said film into said surface of said solid polymer electrolyte to cure said film and adhere said film to said surface; and

removing said release blank from said film.

12. A method according to Claim 11, wherein the step of dispersing said catalyst in said ionomer further includes the steps of:

05 adding a solvent to said ionomer and said catalyst to obtain a mixture with a viscosity effective for forming said film; and

agitating said mixture to disperse said catalyst.

13. A method for fabricating a gas reaction fuel cell having a solid polymer electrolyte membrane for separating anodic and cathodic electrodes, comprising the steps of:

05 furnishing a perfluorosulfonate ionomer in a  $\text{Na}^+$  form;

uniformly dispersing a supported Pt catalyst and a solvent in said  $\text{Na}^+$  form of said ionomer to form an ink;

10 forming a layer of said ink containing a predetermined amount of said catalyst on a surface of said solid polymer electrolyte membrane;

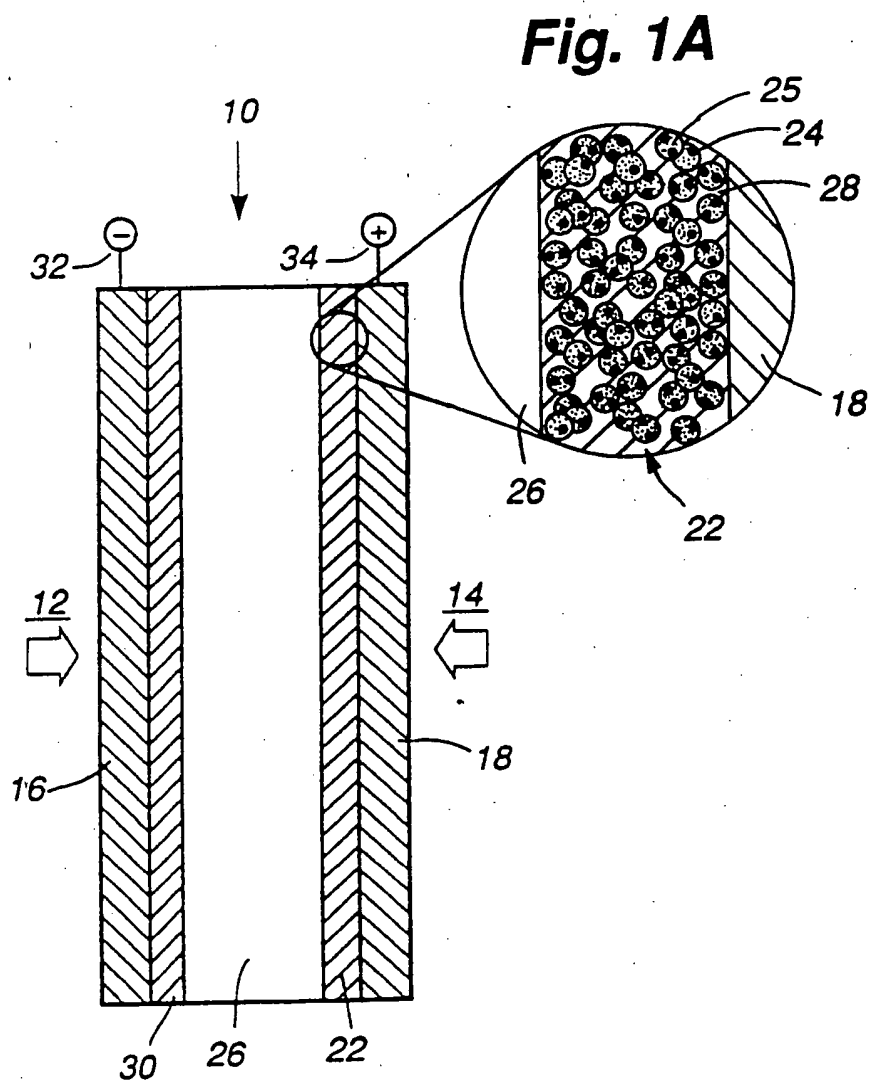
heating said layer of said ink to a temperature of at least  $150^\circ\text{C}$  for a time effective to dry said ink; and

converting said  $\text{Na}^+$  form of said perfluorosulfonate ionomer to a protonated form.

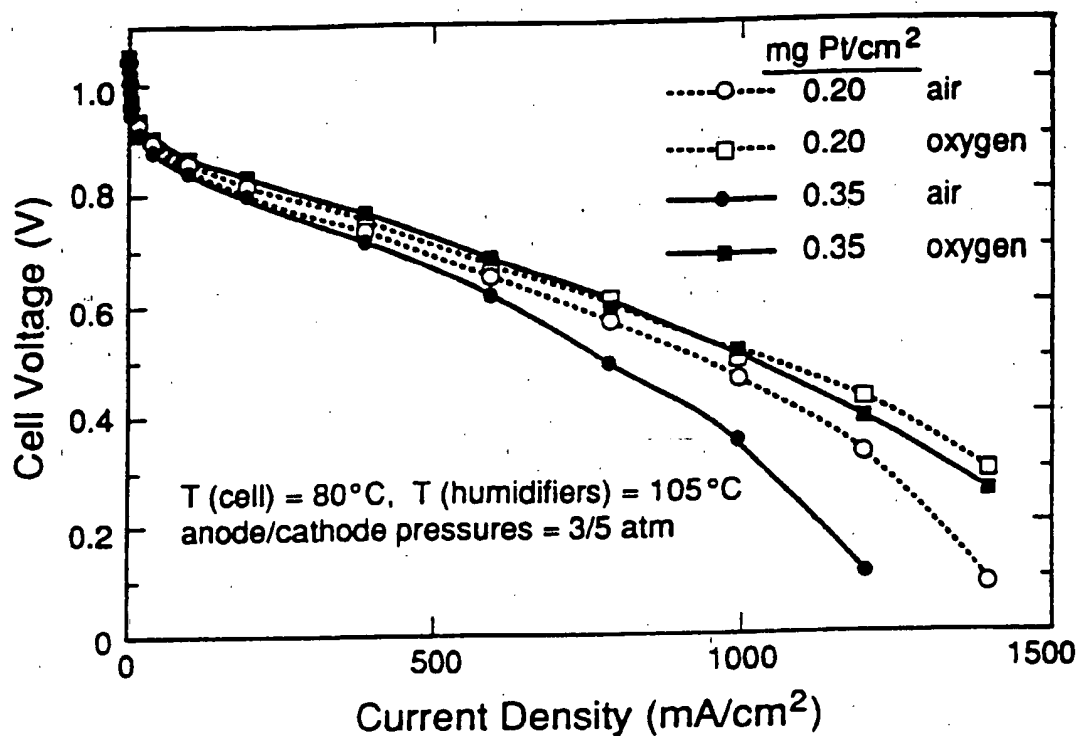
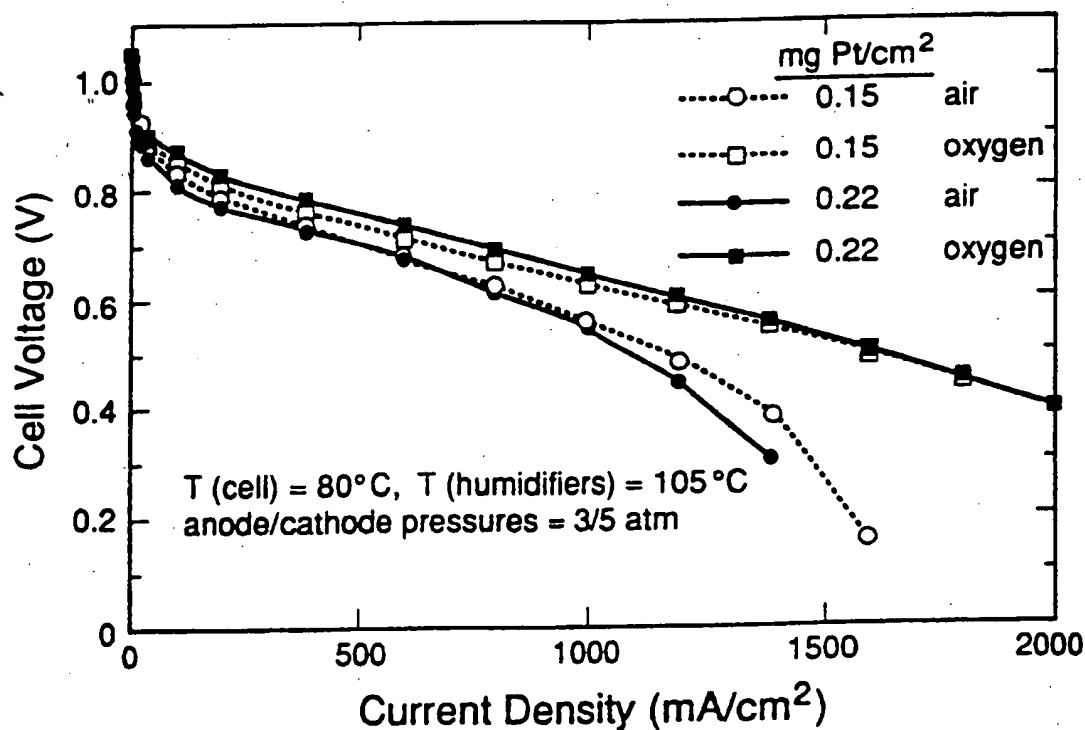
14. A method according to Claim 13, wherein the step of furnishing said perfluorosulfonate ionomer in a  $\text{Na}^+$  form includes the step of adding NaOH to a protonated form of said perfluorosulfonate ionomer.

15. A method according to Claim 14, further including the step of furnishing said solid polymer electrolyte membrane in a  $\text{Na}^+$  or  $\text{K}^+$  form.

16. A method according to Claim 13, further including the step of maintaining said membrane planar on a vacuum table while forming said layer of said ink on said membrane.

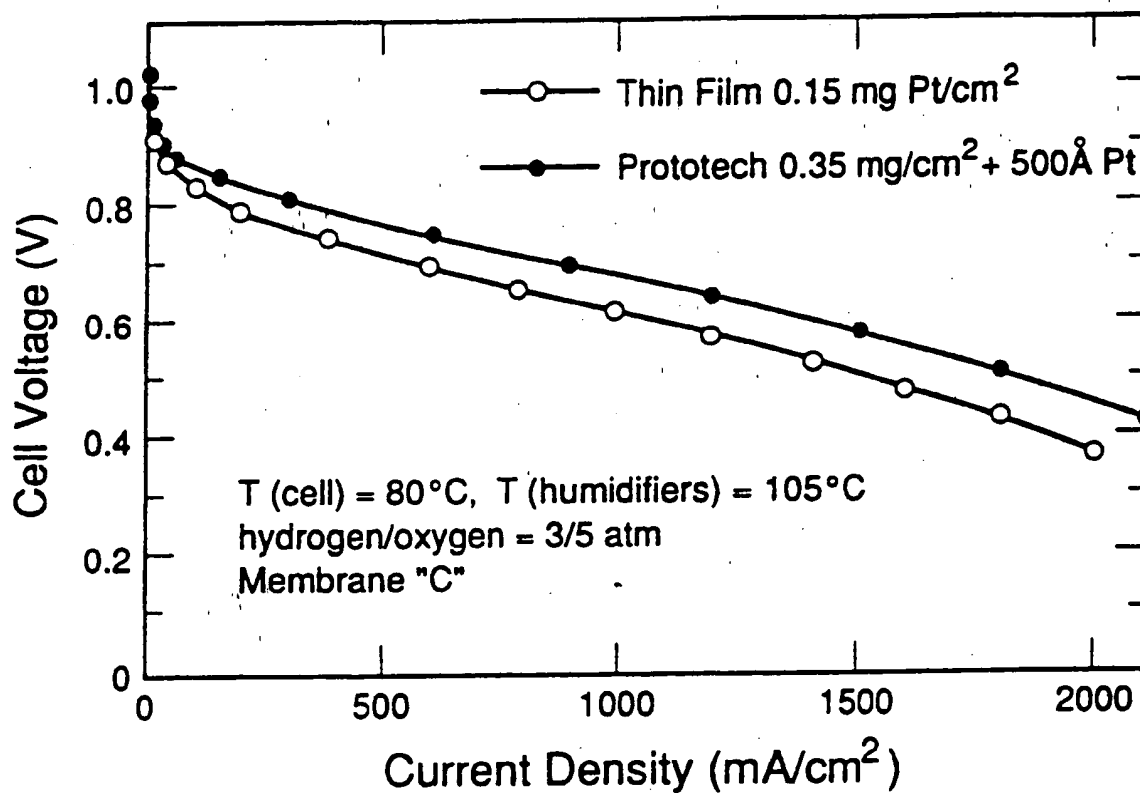
**Fig. 1**

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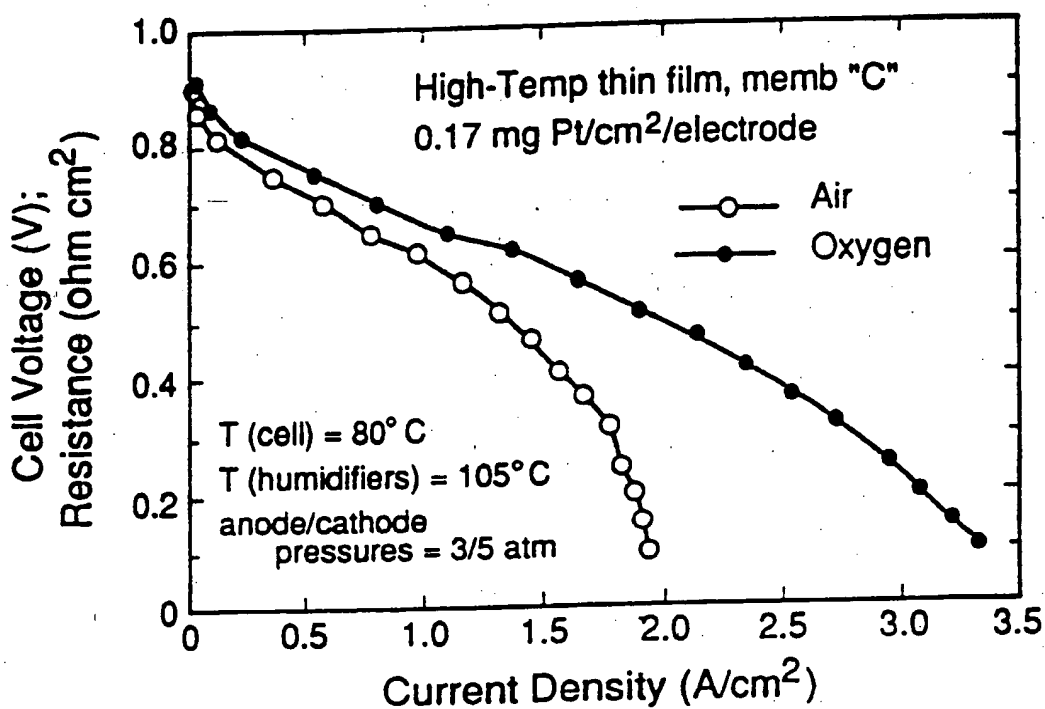
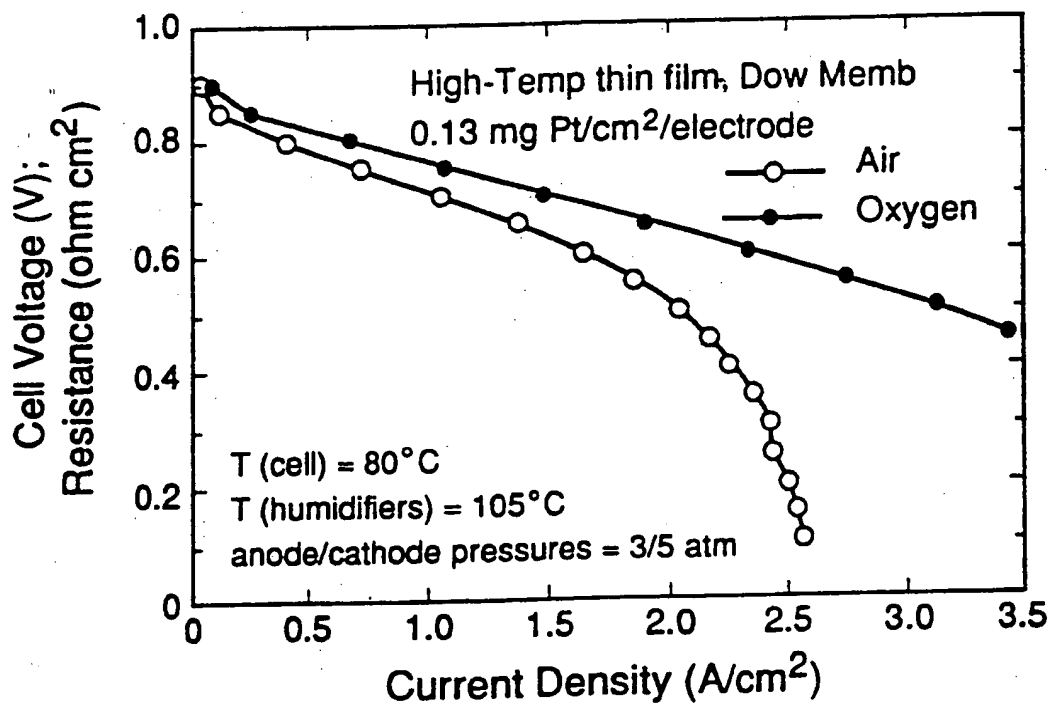
**Fig. 2****Fig. 3**



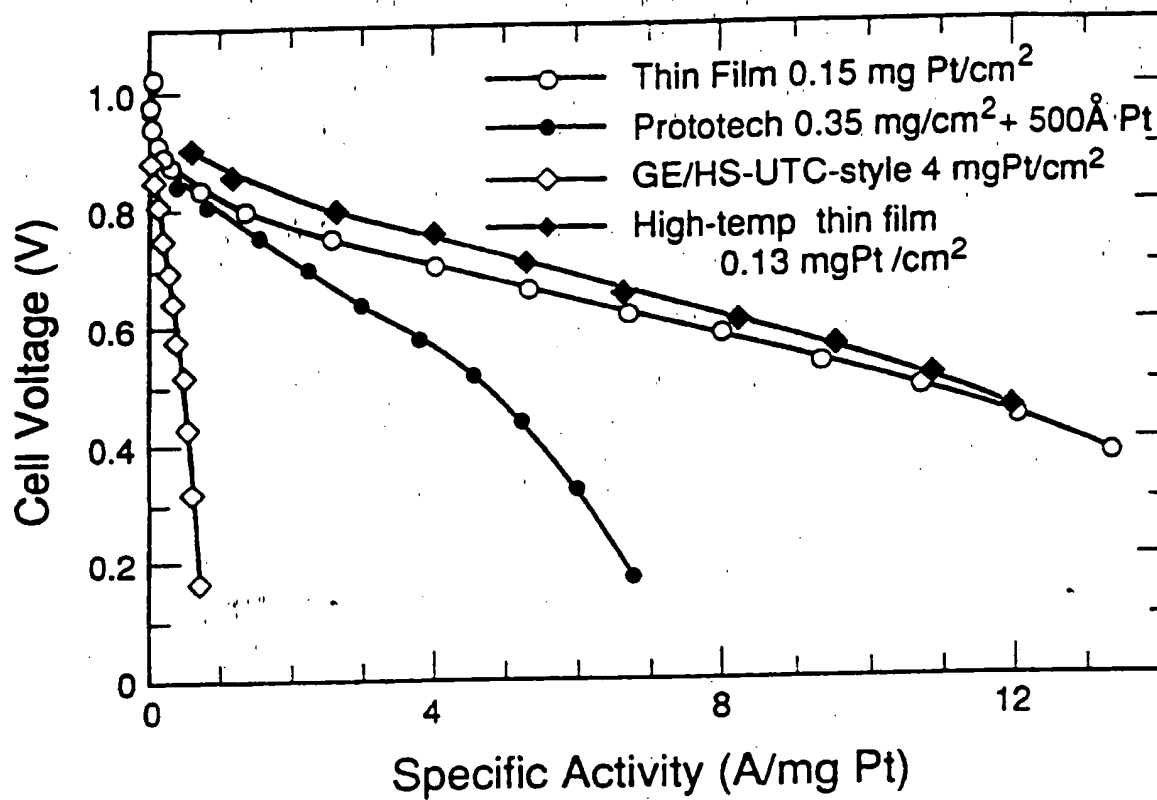
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**Fig. 4**

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**Fig. 5****Fig. 6**

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**Fig. 7**

# INTERNATIONAL SEARCH REPORT

International Application

/US92/01058

## II CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. (5) H01M 8/10  
U.S. CL. 429/33

## III FIELDS SEARCHED

Minimum Documentation Searched

Classification System

Classification Symbols

U.S. 429/33, 42  
427/115

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are included in the Fields Searched

## III DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No. 1
X	US, A, 4,876,115 (Raistrick) 29 October 1989.	1-4
Y	See column 4, lines 36 - 59.	5-16
A	US, A, 4,804,592 (Vanderborgh et al) 14 February 1989. See column 5, lines 14 - 44.	1-16
A	US, A, 4,369,103 (White) 18 January 1983. See the entire document.	1-16
A	US, A, 4,262,063 (Kudo et al) 14 April 1981. See column 3, lines 31 - 40.	1-16

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

\* "later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention"

\* "document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step"

\* "document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art."

\* "A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

Date of Mailing of this International Search Report

21 May 1992

10 JUN 1992

International Searching Authority

Signature of Authorized Officer

ISA/US

Stephen J. Kalafut

Form PCT/ISA/210 (SECOND EDITION) (Rev. 11-87)

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## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,215,183 (MacLeod) 29 July 1980. See column 4, lines 32 - 43.	1-16
Y	Journal of Applied Chemistry, vol. 19, pp. 383-386 (1989). Shulka et al., "A Nation-bound platinized carbon electrode for oxygen reduction in solid polymer electrolyte cells. See page 385, subheading 2.3.	5-16

☒ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

- 1 ☐ Claim numbers \_\_\_\_\_ because they relate to subject matter not required to be searched by this Authority, namely:
  
- 2 ☐ Claim numbers \_\_\_\_\_ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
- 3 ☐ Claim numbers \_\_\_\_\_ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 8.4(a).

☒ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING**

This International Searching Authority found multiple inventions in this international application as follows:

- 1 ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- 2 ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- 3 ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
- 4 ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

**Remarks on Protest**

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication where appropriate, of the relevant passages	Relevant to Claim No.
A	Analytical Chemistry, vol. 58. pp. 2569-2570 (1986): Moore et al, "Procedure for Preparing Solution- Cast Perfluorosulfonate Ionomer Films and Membranes."	1-16